

Reply to Comment on "Theory of Spinodal Decomposition"

S. B. Goryachev
Laboratoire de Métallurgie Physique, Bât. C6,
Université de Lille I,
59655 Villeneuve d'Ascq, France

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In his Comment [1] to my paper [2] Rutenberg notes that "the basis of my analysis of conserved scalar phase-ordering dynamics, to apply only the global conservation constraint

$$\int d\mathbf{x}\psi = N, \quad (1)$$

is incorrect". Because "for physical conserved systems, which evolve by mass transport, the stronger local conservation law embodied by continuity equation"

$$\partial\psi/\partial t = -\nabla\mathbf{j}. \quad (2)$$

This question needs clarification.

Replying shortly, I say that my theory has no any contradiction with the local conservation law (2). It describes the evolution of *all three types* of thermodynamic systems: without conservation law (NCOP), with global conservation law (1) (GCOP) and with local one (2) (LCOP). In these all cases the order parameter (OP) $\delta\psi(\mathbf{x}, t) = \psi(\mathbf{x}, t) - \psi_0(\mathbf{x})$ dynamics near the extremal $\psi_0(\mathbf{x})$ is described by the *same* evolution equation

$$\partial\psi/\partial t = -\Gamma\delta\mathcal{F}/\delta\psi \quad (3)$$

with *different* thermodynamic potential functionals $\mathcal{F}\{\psi\}$. For NCOP-system $\mathcal{F}\{\psi\} \equiv F\{\psi\} = \int d\mathbf{x}f\{\psi\}$, where $F\{\psi\}$ is a free energy functional and $f\{\psi\}$ is a specific free energy one. For GCOP- and LCOP-systems $\mathcal{F}\{\psi\} \equiv \Omega\{\psi\} = F - \mu_g N$, where the *constant* μ_g is a global chemical potential defined by (1) and equilibrium condition $\delta\mathcal{F}/\delta\psi|_{\psi=\psi_0(\mathbf{x})} = 0$. The difference between F and Ω is that the conservation law (1) is taken into account. It should be noted that for GCOP and LCOP-systems (1) must be also used directly for selection

of valid solutions of (3). So *there is no difference between GCOP and LCOP evolution*. That is why I have used the same notation (COP) for them in [2].

Writing evolution equation (3) I proceed from classical point of view that a system has a thermodynamic potential $\mathcal{F}\{\psi\}$ *if and only if* it is related to dynamical class of, so called, *potential* systems. For potential systems the OP evolution near the extremal $\psi_0(\mathbf{x})$ is described by the equation (3). More generally, $\mathcal{F}\{\psi\}$ is the system's Lyapunov functional for attractor ψ_0 , if $\dot{\mathcal{F}} < 0$ for $\psi \neq \psi_0$ and $\dot{\mathcal{F}} = 0$ for $\psi = \psi_0$. Dynamics of the potential system consists of relaxation toward the minimum $\mathcal{F}_0 = \mathcal{F}\{\psi_0\}$ and the Lyapunov functional existence guarantees a system's global asymptotic stability at $\psi = \psi_0$. In more physical language the condition $\dot{\mathcal{F}} < 0$ for $\psi \neq \psi_0$ and $\dot{\mathcal{F}} = 0$ for $\psi = \psi_0$ is nothing more nor less than the second law of thermodynamics.

Rutenberg states that (2) applies a supplementary constraint on the OP evolution. It is not right, because for LCOP we can always find from (2) and (3) the OP flux \mathbf{j} , being a priori an *unknown* quantity, by writing a *transport equation* [3, 4]

$$\nabla \mathbf{j} = \Gamma \delta \Omega / \delta \psi. \quad (4)$$

If $\text{rot} \mathbf{j} = 0$, we can rewrite (4) as [4]

$$\mathbf{j} = -\Gamma \nabla \mathcal{M} / (4\pi). \quad (5)$$

Here $\mathcal{M}(\mathbf{x}, t) = \int d\mathbf{x}' \{ [\delta \Omega \{ \psi(\mathbf{x}', t) \} / \delta \psi] / |\mathbf{x} - \mathbf{x}'| \}$ is a non-local characteristic of the system, so called, scalar potential of the vortex-free vector field $\mathbf{j}(\mathbf{x}, t)$ [5].

In linear approximation, when $f = [A\psi^2 + C(\nabla\psi)^2]/2$, we get from (4) and (5)

$$\nabla \mathbf{j} = \Gamma (A\psi - C\Delta\psi), \quad (6)$$

and $\mathbf{j}(\mathbf{k}, \omega) = \omega_\psi(\mathbf{k}) \delta\psi(\mathbf{k}, \omega) \mathbf{k} / k^2$ with $\omega_\psi(\mathbf{k}) = -i\Gamma(A + Ck^2)$. The condition $\mathbf{j}(\mathbf{k}, \omega)|_{\mathbf{k}=0} = 0$ is guaranteed by $\delta\psi(\mathbf{k}, \omega)|_{\mathbf{k}=0} = 0$, which follows from (1). We see that \mathbf{j} consist of *two transport modes*: a *dilatation* one, which corresponds to an extension or a contraction of OP and a *diffusion* one, which corresponds to Fick diffusion. If we suppose that the characteristic time of OP dilatation $\tau_A = 1/(\Gamma A)$ is much greater than the characteristic time of OP diffusion $\tau_C = 1/(\Gamma C k^2)$, i.e. $k^2 \gg 1/\xi^2$ ($\xi = \sqrt{C/A}$ is the correlation length of OP fluctuations), we get Fick's law in its classical form

$$\mathbf{j} = -\mathcal{D} \nabla \psi \quad (7)$$

with the diffusion coefficient $\mathcal{D} = \Gamma C$.

To derive Fick's law in the form

$$\mathbf{j} = -\lambda \nabla \mu_l, \quad (8)$$

where $\mu_l = \mu_l(\mathbf{x}, t)$ is a local chemical potential and λ is a transport coefficient, it is necessary to introduce a *local equilibrium assumption*. Let us divide the

system into cells of a small volume $V_l = l^d$ with $l \ll 1/k$. In each cell the diffusion mode of $\mathbf{j}(\mathbf{k}, \omega)$ dies away after the time $\tau_l = l^2/(\Gamma C)$ much smaller than the relaxation time τ_C of the diffusion mode in the system as a whole. Then we can believe that all local thermodynamic variables and functions as OP ψ , free energy F_l , entropy S_l , pressure P_l , chemical potential μ_l etc. are *constants* in the cell. It is the assumption of local equilibrium that makes possible to meaningfully define the local free energy $F_l(\mathbf{x}, t)$ that is the same function of the local thermodynamic variables as the equilibrium free energy is of the equilibrium thermodynamic parameters. That is why the fundamental differential relation $dF_l = -S_l dT - P_l dV + V_l \mu_l d\psi$ is valid locally. Replacing $F\{\psi\} = \int_{V_l} d\mathbf{x} [A\psi^2 + C(\nabla\psi)^2]/2$ by the local free energy $F_l(\psi) = V_l A\psi^2/2$ and using formulas of traditional equilibrium thermodynamics we can calculate the local chemical potential $\mu_l(\mathbf{x}, t) = dF_l(\psi)/d\psi = V_l A\psi(\mathbf{x}, t)$ and find (8) with $\lambda = \Gamma C/A$ [4]. If we are interested by self-organisation effects, we must consider the situation, where $\xi^2 k^2 \approx 1$ and \mathbf{j} is defined by (6), but not by (7) or by (8).

We see that Fick's law in form (8) is itself a *consequence* of OP evolution equation, so it can not be utilised for its *derivation*. Fick's law in form (7) describes a special case of OP transport: diffusion without dilatation. Fick's law in form (8) is an approximative expression for diffusion flux, not only in the sense that it does not take into account the higher order gradient terms of a chemical potential μ_l , but also in the sense that it is a law of the linear thermodynamics for which the local equilibrium assumption is compulsory. General expression for OP flux (5) has nothing to do with the Fick's law form

$$\mathbf{j} = -\lambda \nabla \delta F / \delta \psi \quad (9)$$

criticized in [2] and accepted in [1] as "motivated phenomenologically". The use of (8) with formally defined "local chemical potential" $\mu(\mathbf{x}, t) = \delta F / \delta \psi$ has no thermodynamic foundation and is incorrect. This completely concerns the equation

$$\partial \psi / \partial t = -\lambda \nabla^2 \delta F / \delta \psi. \quad (10)$$

An origin of the misunderstanding is, as has been note in [2], a false adoption of the Fick's law in form (9) as a fundamental general law, which can be used as a basis for derivation of the OP evolution equation of nonequilibrium thermodynamic systems with COP.

Fick's law (8) fails completely in a non-linear dynamics. In a non-linear approximation, when $f\{\psi\} = [A\psi^2 + B\psi^4/2 + C(\nabla\psi)^2 + D(\Delta\psi)^2 + E(\psi\nabla\psi)^2]/2$ equation (4) has the form

$$\nabla \mathbf{j} = \Gamma [A\psi + B\psi^3 - C\Delta\psi + D\Delta^2\psi - E\psi^2\Delta\psi]. \quad (11)$$

We see that $\nabla \mathbf{j}$ includes now not only the dilatation mode and the diffusion mode, but also a cross term $E\psi^2\Delta\psi$, being responsible for the dilatation - diffusion coupling. In this case we can not in principal separate dilatation and diffusion effects.

Some words about the example given by Rutenberg. It does not show any inconsistency of my theory with the local conservation law (2), but brilliantly demonstrate incorrectness of (10). Let us, following [1], take "a special initial condition" and "require that the dissipative dynamics be invariant under $\psi \rightarrow -\psi$ and that $F\{\psi\}$ is minimized by $\psi = \pm 1$ everywhere except for a small sphere where $\psi = -1$, the other of which has $\psi = +1$ and -1 , respectively". For simplicity, let us omit the gradient term in Rutenberg's free energy functional and take $F\{\psi\} = \int d\mathbf{x}(\psi^2 - 1)^2$. Then the system initial state is evidently an equilibrium one for all three cases NCOP, GCOP or LCOP. Therefore we must not observe any changes of $\psi(\mathbf{x}, t)$ in time. However, following [1], we get from (10) that "the spheres evolve". This is nonsense. This circumstance can be directly discovered from (10), if we note that by the condition $\nabla^2 \delta F / \delta \psi = 0$ it defines a false equilibrium state, being different, in general case, from the real equilibrium one. The later must always minimize $F\{\psi\}$, i.e. must be determined by the condition $\delta F / \delta \psi = 0$.

References

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